USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA

STANDARD OPERATING PROCEDURE 314

LOW LEVEL ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN AIR BY GC/MS SELECTED ION MONITORING

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1 SCOPE AND APPLICABILITY

This Standard Operating Procedure (SOP) describes the analysis of low-level volatile organic compounds (VOCs) in air samples collected in specially prepared stainless steel canisters. This SOP is based on EPA Method TO-15, Second Edition, January 1999. Deviations from Method TO-15 are described in Appendix A. Analytes and quantitation limits (QLs) are listed in Appendix B.

This SOP is applicable to the analysis of VOCs in air and soil vapor at low levels. Refer to USEPA Region 9 Laboratory SOP 311 *Analysis of Volatile Organic Compounds in Air and Soil Vapor)* for the analysis of higher concentration VOCs in air samples.

2 METHOD SUMMARY

A known volume of sample is directed from the sample container through flow controller to a micro-scale purge and trap, separated in the GC column, and detected by a mass spectrometer (MS) operating in the selected ion monitoring (SIM) mode. Three ions are monitored for most compounds. Target VOCs are identified in the sample by analyzing standards under the same conditions employed for samples and comparing the resulting mass spectra and GC retention times in the sample to the mass spectra and GC retention times of the standard. Each target compound is quantitated using relative response factors from the most recent initial calibration.

3 DEFINITIONS

A list of terms and definitions specific to this procedure appears below. For terms and acronyms in general use at the EPA Region 9 Laboratory refer to Appendix A of the Laboratory Quality Assurance Plan.

<u>FC43</u>: Perfluorotributylamine. A compound used to tune the MS.

<u>GC/MS Tuning Solution (MS tune)</u>: Bromofluorobenzene (BFB) used to evaluate the performance of the GC/MS system with respect to a defined set of method criteria.

<u>Selected Ion Monitoring (SIM)</u>: A mass spectrometry scanning mode in which only a limited mass-to-charge ratio range is transmitted and/or detected by the MS, as opposed to the full spectrum range. SIM typically results in significantly increased sensitivity but with reduced specificity compared with full-scan mode.

4 SAFETY & HEALTH

All laboratory personnel must follow health and safety requirements outlined in current versions of the *EPA Region 9 Laboratory Chemical Hygiene Plan* and the *Region 9 Laboratory Business Plan*. Potential hazards specific to this SOP as well as pollution prevention and waste management requirements are described in the following sections.

4.1 Chemical Hazards

Due to the unknown and potentially hazardous characteristics of samples, all sample handling and preparation should be performed in a well-vented laboratory fume hood.

The toxicity and carcinogenicity of each reagent used in this method may not be fully established. Each chemical should be regarded as a potential health hazard and exposure to them should be minimized by good laboratory practices. Refer to the Material Safety Data Sheets located in Room 118 (library) and the LAN at I:\MSDS IMAGES for additional information.

The following analytes covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: Vinyl chloride and trichloroethylene. Primary standards of these toxic compounds are prepared from commercially prepared gas reference standards that are available in various gas cylinder sizes. These standards must be prepared in a hood. If standard preparation is by dynamic dilution of the gaseous contents of a cylinder of stock gas calibration standards, then the dilution system must be vented into a hood.

The procedure described in this SOP involves the use of cryogenic liquids for cooling the Entech concentrator. Region 9 SOP 770, *Handling Cryogenic Materials*, provides guidelines for the safe handling of these materials.

4.2 Equipment and Instruments

Follow the manufacturer's safety instructions whenever performing maintenance or troubleshooting work on equipment or instruments. Unplug the power supply before working on internal instrument components. Use of personal protective equipment may be warranted if physical or chemical hazards are present.

All compressed gas cylinders must be securely chained to laboratory benches or walls and placed so that the labels can be easily read.

Canisters should never be pressurized beyond 45psia, which is the maximum allowable pressure for specially prepared canisters.

4.3 Pollution Prevention

Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA Region 9 Laboratory places pollution prevention as the management option of first choice with regard to environmental management. Whenever feasible, laboratory personnel shall use pollution prevention techniques to address waste generation. When wastes cannot be feasibly reduced, recycling is the next best option. The *EPA Region 9 Laboratory Environmental Management System* provides details regarding efforts to minimize waste.

No solvents are utilized in this method except the very small volumes of methanol needed to make calibration standards. The only other chemicals used in this method are the neat materials in preparing standards and sample preservatives. All are used in very small amounts and pose no threat to the environment.

4.4 Waste Management

The EPA Region 9 Laboratory complies with all applicable rules and regulations in the management of laboratory waste. The laboratory minimizes and controls all releases from hoods and bench operations. All analysts must collect and manage laboratory waste in a manner consistent with EPA Region 9 Laboratory SOP 706 *Laboratory Waste Management Procedure*. Solid and hazardous wastes are disposed of in compliance with hazardous waste identification rules and land disposal restrictions. If additional guidance is needed for new waste streams or changes to existing waste streams, consult with EPA Laboratory Safety, Health, and Environmental Manager (LaSHEM) or ESAT Health and Safety and Environmental Compliance Task Manager or designees.

This procedure generates the following waste streams:

Waste Stream Description	Waste Label	Hazard Properties
Laboratory solid waste (gloves, contaminated paper towels, disposable glassware, etc.)	Non-hazardous Waste	Not applicable
Methanol waste (methanol, halogenated volatile compounds)	Hazardous Waste	Flammable, toxic
Spent stock standard cylinders (Depleted or Expired: Must be vented to ambient pressure in fume hood prior to disposal)	Recycled / Non-hazardous Waste	Not applicable

Stock standard cylinders purchased from Restek Corporation (Spectra Gases, Inc.), when ready for disposal, are vented in a fume hood to ≤ 15 psig, labeled "EMPTY", and are returned to the manufacturer: Environmental Division, Spectra Gases Inc., 80 Industrial Drive, Alpha NJ, 08865.

Stock standard cylinders purchased from Supelco (Sigma-Aldrich), when ready for disposal, are vented in a fume hood to ambient pressure, labeled empty, made unusable by drilling a hole through the cylinder, and disposed of with the non-regulated waste.

5 SAMPLE HANDLING AND PRESERVATION

5.1 Containers and Required Sample Volume

Canisters included are SilcoSteel® silica coated interior canisters, TO-Can^{J} electro polished interior canisters, and Silonite^{TM} coated interior canisters. Analysis of 400 mL sample load volume represents an undiluted sample (i.e. Dilution Factor = 1). Canister sizes vary from 400-mL to 6-L.

5.2 Internal Chain-of-Custody

After samples are received and logged into the Laboratory Information Management System (LIMS), they are delivered by the Sample Custodian to Room 203.

Verify sample IDs and dates and times of collection against the chain-of-custody form. If discrepancies are noted, inform the sample custodian.

Check the following information to ensure that the information on the sample containers corresponds to the information on the tracking sheets and the chain-of-custody record.

- EPA work order number
- Laboratory ID number.
- Case number.
- Sample delivery group number

Sample canisters should have pressures below ambient upon receipt if passive flow controllers were used. Pressure verification is first done by the sampler in the field to ensure the canister has not leaked prior to sampling. Sampler records pre- and post-sampling pressures on the Chain of Custody by reading the gauge attached to the canister. Confirm that the integrity of the canister samples has not been compromised by checking the initial and final pressure of the canisters prior to and after receipt. Canister pressure is checked during sample pressurization step and the pressure reading is compared against the pressure recorded on the COC in the field. Note any problems in the LIMS work order memo field as well as in the Canister Dilution Log.

5.3 Sample Storage

Sample canisters are stored in the air analysis laboratory, room 203 at ambient temperature.

Sort samples according to date sampled, so that samples can be analyzed in order of date sampled to prevent missed holding times. Review due dates and project notes to prioritize RUSH samples (while meeting all sample holding times).

Upon completion of the analysis for an SDG the sample canisters for the entire SDG shall be stored, for a period of 7 days after the SDG is reported. After 7 days, the canisters shall be vented in the fume hood and cleaned as specified in EPA Region 9 Laboratory SOP 312, *Cleaning and Certification of Specially Prepared Canisters for Air Sampling*. If this requirement jeopardizes the supply of clean canisters to field samplers the Chemistry Technical Director must be notified and permission to clean canisters prior to the 7-day courtesy hold requested.

5.4 Holding Time

Samples must be analyzed within 30 days from collection.

6 INTERFERENCES

Contamination may occur if canisters are not properly cleaned. Before each use, canisters must be thoroughly cleaned and certified as outlined in SOP 312.

The cleaning apparatus, sampling system, and analytical system should be assembled of clean, high quality components.

Canisters should be capped tightly during shipping to prevent leakage and sample contamination.

Impurities in the calibration dilution gas and carrier gas, organic compounds outgassing from the system components ahead of the trap, and solvent vapors in the laboratory account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running humidified zero grade air instrument blanks. Zero air should be humidified with organic free water that has been prepared according to USEPA Region 9 Laboratory SOP 205, *Preparation of Organic-Free Method Blank Water*. The use of non-chromatographic grade stainless steel tubing, non-PTFE thread sealants, or flow controllers with rubber components must be avoided.

Significant contamination of the analytical system can occur whenever samples containing high VOC concentrations are analyzed. Whenever an unusually concentrated sample is encountered (i.e. concentrations significantly greater than the calibration range of the instrument, often indicated by poor chromatographic peak shape) it should be followed by analysis of zero grade air instrument blank to check for carry-over contamination.

Solvents and other compounds that are target analytes must never be introduced into the laboratory where volatiles analysis is performed. Methylene chloride, acetone, and other common laboratory chemicals that are target analytes analyzed on this system must be excluded from the room where the analysis is performed.

The analytical system is sensitive to water and the amount of humidity in a sample can affect the recovery of target analytes. Conditions of high humidity or water (i.e. rain) should be noted in the chain of custody and mentioned in the case narrative.

Contamination from field samples can build up in the manifold system. The manufacturer recommends flushing the system using the flush routine at the start of every week when the system is actively utilized. Refer to the system manual for additional details.

7 APPARATUS AND MATERIALS

This section describes recommended apparatus and materials to be used for the analysis. All equipment, reagents, standards, and supplies must meet the technical and QC requirements of the reference method. Substitutions may be made provided that they are documented and equivalency is maintained.

7.1 Instruments and Equipment

- GCMS System

  Gas Chromatograph (GC): Hewlett Packard/Agilent 6890 or 6890N, or equivalent. The GC must be capable of multilevel temperature programming and constant carrier gas flow throughout the temperature range. The GC should be equipped with electronic pressure control (EPC).

  Column: RTX624, 60 m length, 0.32 mm ID, 1.8 micron film capillary column, (Restek catalog # 10972) or equivalent. Any column capable of separating the target analytes and passing method QC without overloading at the concentration of the highest standard may be used.

  Mass spectrometer: Hewlett Packard/Agilent 5973 or 5973N, or equivalent, capable of scanning from 35 to 500 amu every one second or less using 70 volts (nominal) electron energy in the electron impact ionization mode. The MS must be able to produce a mass spectrum that meets acceptance criteria when 50ng or less of BFB is introduced into the GC system.

- Data system:

  Agilent ChemStation or equivalent. Able to control the GC/MS system and to acquire, store, and reduce mass spectral data. The software must be able to process any GC/MS data file by recognizing a GC peak within a retention time window, comparing the mass spectrum from the GC peak with spectral data in a database, and generate a list of tentatively identified compounds with their retention times and scan numbers. The software must also allow integration of the ion abundance of any specific ion between specified time and scan number limits and to calculate RRFs and concentrations of analytes in samples.

- Cryogenic Concentrator: Entech 7100A pre-concentrator, or equivalent.

- Autosampler: Entech 7016 Ambient canister autosampler, Entech 7032-L Ambient canister autosampler, or equivalent. This system allows for the sequential analysis of up to 16 canisters.

- SUMMA Canisters: Polished canister with SilcoSteel coated interior, Entech part and part number 01-10622 (6 L) size, or equivalent.

- MiniCan: 400 mL SUMMA canister equipped with quick-connect fittings and Silonite lining, Entech part number 29-MC400S or equivalent. The can should also be equipped with a MiniCan Cap to protect the quick connect valve during shipping, Entech part number 29-CAP-CH or equivalent. In general, 400-mL canisters are only used when project specific information indicates that all project requirements can be met with a reduced sample volume.

- Diluter: Entech 4600 dynamic diluter or equivalent. This system is used to create calibration standards by diluting stock standards. It is also used in diluting samples. The diluter uses Mass Flow Controllers to perform the dilutions.

- Canister cleaner: Entech 3100A Canister Cleaner or equivalent and associated equipment.

Other GC/MS, concentrator, or autosampler systems with similar configurations can be used to analyze samples following this SOP as long as the instrumentation has been demonstrated to meet the QC limits of this SOP.

7.2 Reagents

The following reagents are to be used at the specified or higher grade:

- Helium gas — (Ultra High Purity)
- Liquid nitrogen (50 psig and 350 psig)
- Nitrogen gas
- Air, Zero Grade (e.g. Praxair Part # AI 0.0Z)
- Organic-free water (EPA Region 9 Laboratory SOP 205 *Preparation of Organic-free Method Blank Water*)

Reagents may contain impurities that affect analytical data. If the purity of a reagent is in question, analyze for contamination prior to use.

7.3 Standards

When ordering standards from various suppliers it is important to determine that the primary and secondary sources are truly independent. Experience has shown that suppliers frequently purchase gas phase standards from outside sources. For example, supplier A may ship lot #1; supplier B ships lot #2, but both suppliers purchased the cylinders from supplier C who only prepared one lot.

All stock standards upon receipt must be recorded into the LIMS and assigned a standard ID number. Sources, expiration dates, components, and concentrations for gas mixtures must be recorded onto the LIMS. Standard ID number and expiration dates must be printed on to the standard cylinder's label. Store all standards at room temperature.

Working standards should be allowed to equilibrate for at least 2 hours after preparation prior to use. Store air standards at room temperature.

Stock Standards - Stock standard solutions may be purchased as certified mixtures or prepared from ACS reagent grade materials.

- Internal Standard Gas Mixture - commercially prepared certified custom gas mixture containing the following with nitrogen making up the balance: bromochloromethane, chlorobenzene-d5, and 1,4-difluorobenzene. Restek/Spectra Gases TO-14A mix, catalog no. 34427 (100 ppbv), catalog no. 34412 (1 ppmv), or equivalent.

- 4-Bromofluorobenzene Tuning Standard - commercially prepared certified gas standard containing nominally 100 ppbv of BFB that is equivalent to 0.78 ng BFB per mL of standard mix. Restek catalog no. 34424 (100 ppbv), Restek catalog no. 34406 (1 ppmv), or equivalent.

$$\frac{175\, g_{BFB}}{mole_{BFB}} \times \frac{100 \times 10^{-9}\, moles_{BFB}}{mole_{Nitrogen}} \times \frac{1 \times 10^{9}\, ng_{BFB}}{g_{BFB}} \times \frac{mole_{nitrogen}}{24{,}470\, mL_{Nitrogen}} = 0.715\, ng_{BFB}/mL$$

- Calibration Gas Standard (stock) - commercially prepared certified gas standards containing target compounds.

  Primary list- Scotty (Air Liquide) TO-14A 39 Component Mix, l00 ppbv in nitrogen, Supelco catalog no. 41900-U or equivalent.

  Subset list- Scotty (Air Liquide) TO-15 Subset 25 Component Mix, 100 ppbv in nitrogen, Supelco catalog no. 41979-U, or equivalent.

  Additional list- commercially prepared certified custom gas standards containing target compounds that maybe needed for a specific project.

- Second Source Verification(stock) Primary list- commercially prepared certified custom gas standard containing target compound derived from a secondary source or different standard lot, depending on commercial availability.

  Primary list- Restek/Spectra/Linde TO-14 43 Component Mix, 1 ppmv in nitrogen, catalog no. 34433 or Restek/Spectra/Linde TO-14 Component Mix, 100 ppbv in nitrogen, catalog no. 34432, or equivalent.

  Subset list- Restek/Spectra/Linde 25 Component Mix, l ppmv in nitrogen, catalog no. 34434; TO-15 Restek/Spectra/Linde 25 Component Mix, 100 ppbv in nitrogen, catalog no. 34435; or equivalent.

  Additional list- Commercially prepared certified or in-house custom gas standards containing target compounds that maybe needed for a specific project.

- Preparation of Working Calibration Standard

  Calibration gas standards are prepared by diluting as necessary commercially prepared certified gas standards that typically contain l00 ppbv of each target compound (stock standard). A single working standard at 400 pptv is prepared from which calibration can be derived by varying the sample volumes loaded during the pre-concentration step.

  Note: The concentrations of the calibration levels may be modified to achieve a desired calibration range as long as they meet QA/QC criteria as stated in Section 8 of this SOP.

  The concentration of the working standard is calculated using the following equation:

  $$C_F = C_I\,(f_i / f_t) = C_I\,(f_i / f_d + f_s) \text{ since } f_t = f_d + f_s$$

Where:
C_F is the final concentration of the working standard
C_I is the initial concentration of the calibration standard
f_i is the flow rate from the calibration standard
f_d is the flow rate of the dilution gas (humidified zero air)
f_s is the sum of all flow rates
f_t is the total flow rate

- In-House Prepared Calibration Standards –

  Standards may be prepared in-house using the procedure outlined in Appendix E.

- Second Source Calibration Verification Sample (SCV) –

Approximately equivalent to the mid-point initial calibration solution but prepared from a source different from the source of the calibration standards. The SCV is used to check the accuracy of the initial calibration solutions. See table below for suggested vendors for SCV standards.

7.4 Supplies

- Stainless steel tubing and stainless steel fittings.
- Stainless steel cylinder pressure regulator: standard two-stage cylinder regulators with pressure gauges.
- Gas-tight syringes (1-mL, 5-mL, 25-mL and 50-mL).

8 ANALYTICAL PROCEDURES

8.1 Instrument Operation

Check the mass spectrometer for leaks on a daily basis using the instructions provided in Appendix D. Generate and print a leak check report and include in the data package.

Set up the Entech autosampler parameters according to parameters in Appendix D.

Set up the GC/MS following operating instructions provided by the manufacturer. Use the operating parameters provided in Appendix D as a starting point. Recommended compound groups and primary and secondary ion assignments are provided in Appendix D.

8.1.1 GC/MS tuning:

Mass calibration of the analytical system must be performed prior to an initial calibration, whenever the source is cleaned, or whenever a mass miss-assignment is noted. Mass calibration is performed to ensure the accurate assignment of masses to ions. Use perfluorotributylamine (FC43) to perform mass calibration of the instrument.

Calibrate the Mass Axis of the MS prior to analyzing the BFB standard. Use the settings in the most recent tune file as the initial conditions; save the tune file using the naming convention in Appendix I and generate a tune report.

Refer to Appendix C acceptance criteria and corrective action requirements.

8.1.2 GC/MS System Performance Check (BFB analysis)

The GC/MS system must meet the mass spectral ion abundance criteria for BFB prior to analysis. Proper tuning of the instrument is necessary to produce standardized fragmentation patterns of target compounds.

Introduce approximately 30 ng of BFB onto the analytical system using the operating parameters provided in Appendix D. BFB is normally injected along with the system priming (high level standard). The priming standards is also used to ensure that retention time for target analyst has not drifted which may cause target analytes to drift outside the rendition time/SIM acquisition window.

The autofind procedure will automatically find the BFB peak, average three scans (the peak apex scan and the scans immediately preceding and following the apex), perform a background subtraction, and print out a hard copy of the spectrum, the chromatogram, and the table of ion abundances.

Refer to Section 9.2.1 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

Save the method using the naming convention in Appendix I.

8.2 Calibration and Standardization

8.2.1 Initial Calibration

The GC/MS system must is calibrated at five concentrations that span the monitoring range of interest.

The recommended nominal concentrations are listed in the following table. Source standard certified concentrations vary slightly and are used to calculate accurate actual concentrations for each calibration.

Calibration Level	Concentration, pptv	Internal Gas Standard Mix, 400 pptv, mL	Calibration Standard Mix, 400 pptv, mL
1[1]	50	50	50
2	150	50	150
3[2]	250	50	250
4	350	50	350
5	500	50	500

[1] QLS
[2] CCV or LCS

Check the initial calibration for misidentified peaks due to retention time shifts. Review quantitation ions to assure that none saturates the detector.

The data system calculates the relative response factor (RRF) for each target compound for all calibration standards using the following equation. The quantitation ions and internal standard assignments are listed in Appendix C.

$$RRF = (A_x)(C_{is})/(A_{is})(C_x)$$

Where

A_x = Area of quantitation ion of compound x
A_{is} = Area of quantitation ion for associated internal standard
C_x = Concentration of compound x
C_{is} = Concentration of the associated internal standard

Check and print the calibration by performing the following steps:

1. In the ChemStation data analysis module, load the current initial calibration method from C:\ MSDCHEM\Year\Methods\ or D:\MSDCHEM\Year\Methods\
2. Perform an initial calibration using the recommended concentrations listed in above.
3. Update the response factors in the method using the newly acquired calibration files.
4. Update the retention time in the method using the newly acquired continuing calibration level.
5. Update the qualifier ion relative responses from the CCV calibration level.
6. Save the method as outlined in the " ChemStation File Naming Convention" (see Appendix I)
7. Generate "Response Factor Report."
8. Check the calibration files listed on the "Response Factor Report" to insure that the correct files are being used.
9. Check the time and date to ensure that the correct update is used.

10. Process the SCV with the newly created initial calibration, check to make sure the "QLast Update" time and date match the "Response Factor Report"
11. Open and immediately close ChemStation Custom Reports. (Note: no ChemStation custom reports are actually used, opening and closing custom reports populates "detail.xls" which is later mined for data.)
12. Open the latest copy of Custom Report. Make sure automatic updates of links is enabled under options.
13. Go to the "SCV Recovery", "ICAL Area", "ICALconc", tabs and print reports. Make sure the SCV passes acceptance criteria (Appendix C) and the ICAL areas match what is on the ChemStation quant reports.
14. Verify that the method was updated correctly. Print the Compound List Report from ChemStation. Verify that the average response factor is used. Scrupulously check the elution order and retention times, compare them to an old ICAL if needed.
15. Copy the method to LAN as outlined in the "ChemStation File Naming Convention"
16. Save a hard copy of the initial calibration files so they may be copied and included in associated packages.

The analyst should demonstrate that all parts of the equipment in contact with the sample and reagents are not contaminated. This is accomplished through the analysis of a method blank or an instrument blank.

Refer to Section 9.2.2 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

Calibration note: on occasion, an analytical system calibrated for a specific project must be used to analyze samples requiring additional compounds. Additional calibration standards may be analyzed and added to the method. The method update must be thoroughly documented. Note that the internal standards in the method will be those acquired during the first analyses and the RRFs for the additional compounds will use the earlier internal standard area count. Therefore, it is important that the internal standards of the added calibration points demonstrate similar response to prevent significant error in the RRFs used for quantitation.

8.2.2 Continuing Calibration

A continuing calibration standard at a mid-level concentration must be analyzed. On the day an ICAL is acquired, the mid-level calibration standard shall act as the CCV when samples are analyzed within the same 24-hour period as the ICAL.

Note that CCV and LCS/BS are the same and that one analysis can serve both functions (i.e. instrument calibration verification and batch accuracy QC).

1. In the ChemStation data analysis module, load today's method from D:\MSDCHEM\Year\Methods.
2. Acquire the continuing calibration using today's method.
3. Quantitate the continuing calibration file.
4. Generate "Evaluate Continuing Calibration Report".
5. Compare the IS retention times and areas in the CCV standard to the mid-point standard of the most recent initial calibration. Adjust the electron multiplier (EM) voltage if needed (an increase of 50 volts will typically double the response). If the EM voltage is changed, reanalyze BFB and the CCV.
6. As each run is quantitated during the day, make sure that the same date and time stamp, (e.g. "QLast Update: Mon Jul 25 08:15:58 2011"), is recorded on each file header.
7. If QLast Update time stamp changes, state the reason, repeat steps4 through 7 above, and include the reports generated in the package.
8. Save a copy of the method to the LAN, when the data are backed up to the LAN the following day.

Refer to Section 9.2.3 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

8.1.3 Quantitation Limit Verification Standard (QLS)

Analyze a quantitation limit standard at the concentration of the lowest point of the initial calibration.

Use the ChemStation custom report (Full_custom_report to calculate the QLS recoveries.

Refer to Section 9.2.4 and Appendix C for acceptance criteria and corrective action requirements.

8.3 Analysis

Sample canister pressures are checked and recorded by the analyst upon receipt in room 203 using the Entech 4600 dynamic diluter. Canisters are typically pressurized to a 1.5x dilution in order to bring canister pressures above ambient (approximately 15 - 25psia). Dilution procedures and calculations are recorded in the Dilution Logbook. Record canister number, initial canister pressure, final canister pressure, and the ambient pressure readings in the dilution logbook. An example of the Dilution Logbook is provided in Appendix F.

8.3.1 Sample Preparation

Check that the serial numbers on the canisters coincide with the numbers on the routing forms to ensure that the correct sample is being analyzed.

Check the canister pressure and record the initial canister pressure, final canister pressure, and the ambient pressure readings in the Dilution Logbook even if sample dilution is not necessary. An example of the Dilution Logbook is provided in Appendix F.

If sample canisters are < 10 psia, pressurize canister using a 1.5X dilution factor. Final pressure should be in the 15-25 psia range. Adjust dilution factor to attain a final pressure in this range.

If sample pressure is >10 psia, it may be analyzed without dilution; therefore, the sample need not be pressurized. Record the initial pressure reading in the dilution log regardless if dilution is performed or not.

Prior to analysis, samples must be allowed to equilibrate in the lab for at least 2 hours after their collection or after a dilution has been completed.

If samples are expected to be highly contaminated or are of unknown concentration, screen the samples to 1) protect the analytical system from damage or contamination and 2) to determine the appropriate subsequent dilutions. If the sample history is known, select the appropriate dilution to stay within the instrument calibration range.

8.3.2 Sample Dilution

If the on-column concentration of any target compound in any sample exceeds the initial calibration range, a dilution of the sample should be analyzed. Use the results of the original analysis to determine the approximate dilution factor required to get the largest analyte peak within the initial calibration range.

When possible, choose a dilution factor that keeps the response of the largest target compound in the upper half of the initial calibration range of the instrument.

Dilution of the sample can be accomplished by reducing the sample volume taken during the pre-concentration step; however, a sample volume lower than 10 mL is not recommended.

Enter the sample volume utilized in the "initial sample volume" column of the LIMS bench sheet. Final Volume is 400 mL which is the default sample aliquot.

Method detection limit is preserved by analyzing 600 mL of a 1.5 times dilution following pressurizing the canisters.

Dilutions can also be performed by varying the sample load volumes through the Entech 7100 pre-concentrator. This type of dilution is typically performed if target compounds in any sample exceed the initial calibration range. These dilutions are recorded electronically in the Entech sequence log and in the LIMS system.

Dilution may also be accomplished by re-pressurizing sample canisters. Sample dilution factor is calculated by the dynamic diluter as follow:

DF = Pf/Pi where
DF: Dilution Factor
Pf: Final canister pressure
Pi: Initial canister pressure

If further dilution is necessary, an aliquot of the original sample should be taken and diluted into a certified clean canister with zero air. Pressurize the certified canister to 10-15 psia. Draw a known volume aliquot from the sample canister and inject the aliquot in the dilution can. Measure the final can pressure and record the reading in the "final" pressure column of the Dilution Logbook. For samples diluted in secondary canisters, the dilution factor is calculated as follow:

DF = (Pf*Vi)/(Pi*Vf) where
DF: Dilution Factor
Pf: Final canister pressure
Vi: Volume of aliquot
Pi: Ambient pressure
Vf: Final volume (i.e. 400 mL for 400 mL cans)

Record canister number, initial canister pressure, final canister pressure, and the ambient pressure readings in the Dilution Logbook.

The diluted sample should be allowed to equilibrate for 2 hours after preparation before analysis.

In the case of extremely contaminated samples, several dilutions and volume variations may be required. Analysis under USEPA Region 9 Laboratory SOP 311 *Analysis of Volatile Organic Compounds in Air and Soil Vapor* should also be considered for these samples.

8.3.3 Sample Analysis and Analytical Sequence

This section describes setting up the analytical sequence and performing the instrumental analysis. Record the analytical sequence in the instrument run log and the LIMS sequence page.

Load the samples in the autosampler according to their designated positions in the sequence file. The following steps represent the recommended analysis sequence:

1. BFB/Primer
2. CCV/LCS
3. CRL (QLS)
4. MB
5. Samples
6. Sample dilutions, as needed
7. Instrument Blanks, as needed

Enter sample sequence in the instrument software. Include the Laboratory ID (WO-sample number) in the "Sample" field and dilution level, if any, in the "Multiplier" field.

Name the data files according to the data file naming convention outlined in Appendix I.

8.3.4 Instrument Blanks

In the event that a sample is analyzed which exceeds the calibration range of the instrument, an instrument blank should be analyzed to demonstrate that the system is free of carryover contamination.

At a minimum, the analyst must evaluate the next sample to determine if carryover may have occurred by either:

- Analyze an instrument blank immediately after the contaminated sample.
- Monitor the sample analyzed immediately after the contaminated sample for all compounds that were in the contaminated sample that exceeded the limits above.

The instrument blank is acceptable if it meets criteria listed in Appendix C.

Instrument blanks may be analyzed beyond the 24-hour tune time period.

8.3.5 Analyte Identification and Quantitation

- Analyte Identification

In order for a target compound to be identified as present in a sample, both the retention time and the mass spectra of the peak must match those of the standard. Large drifts in retention time may cause target analytes to drift outside the retention time/SIM acquisition window. If large drifts occur, the source of the problem must be identified and corrected.

The relative intensities of the ions must agree within 15% between the continuing calibration verification and sample spectra for all compounds except vinyl chloride and dichloromethane which must agree within 25%.

If a compound cannot be verified by these criteria but is present in the technical judgment of the analyst, the supporting evidence must be indicated on the raw data and the analyte reported.

- Analyte Quantitation

Quantitate the data and print out a quantitation report and chromatogram. Use the average relative response factor from the initial calibration for quantitation.

Review the results for qualitative identification of target analytes as discussed in Analyte Identification, above. Cross out all reported hits that do not meet the qualitative criteria and delete the compound (Qdel) in ChemStation. Review all target compounds that are detected to verify they are integrated properly. Review the chromatogram for possible false negatives.

Check the sample's internal standard recovery with criteria in Appendix C.

8.3.6 Manual Integration

Where the chromatography software integrates the signal inconsistently, follow EPA Region 9 Laboratory SOP 835 *Chromatographic Integration Procedures*. All manual chromatographic integration must be initialed and dated by the analyst and approved by the supervisor, Chemistry Technical Director, Quality Assurance Officer, or designees.

8.3.7 Calculations

Results for target analytes are calculated using the following equation:

$$(C_x) = (A_x)(C_{is})(DF)/((A_{is})(RRF))$$

Where

C_x	=	Concentration of compound x
A_x	=	Area of quantitation ion of compound x
C_{is}	=	Concentration of the associated internal standard (5 µg/L)
DF	=	Dilution factor
A_{is}	=	Area of quantitation ion for associated internal standard
RRF	=	Analyte average relative response factor from the initial calibration

8.3.8 Data and QC Review

As soon as possible after analysis (typically prior to entry into LIMS), inspect sample and QC data for compliance with QC limits in Appendix C. If no significant problems are found, perform the following QC reviews for compliance with SOP requirements:

- Check that target analyte results are within range of the initial calibration.
- Process and review the results for the IB/MB, CCV/QLS, QLS, and instrument QC samples. Print a ChemStation Evaluate Continuing Calibration Report using the appropriate settings to verify that the CCV, QLS, and instrument QC results are within QC limits. See Section 9.2 for instrument QC requirements.
- Process and review the results for the MB, LCS, and Duplicate batch QC samples and verify that the results are within QC limits. See Section 9.3 for batch QC requirements.
- Review all sample results to determine if any samples need to be re-analyzed at a dilution.
- Review the chromatogram for possible false negatives.
- Manually cross out all compounds that do not meet qualitative criteria and document the reason on the quantitation report. Delete the compound (Qdel) in ChemStation.
- If a run is rejected for any reason, mark the raw data “Not Used” in large print and document the reason on the quantitation report.

8.3.9 Data Export and LIMS Entry

Export data from the instrument into text files. Import into the LIMS using DataTool. Review final results in the LIMS.

The LIMS will report two significant figures and detected results to one-half the QL. The LIMS will flag values between one-half the QL and the QL as estimated (J). The analyst must manually add a qualifier flag (C1) indicating that the reported concentration is estimated because it is less than the quantitation limit. Qualify data based on QC results and guidelines in the EPA Region 9 Laboratory QA Plan.

- Generate epatemp.txt files for field and QC samples by printing the report to the screen; these files are used by the LIMS DataTool module to import the instrument results into the Data Entry/Review table.

- Copy sample data files from the local drive to the appropriate instrument data subdirectory on the Region 9 LAN to make them available to LIMS and to archive them.

- Create an empty upload file containing the samples analyzed in the LIMS batch or sequence. Import and merge the data files using the LIMS DataTool module. Load the resulting merged data file into the LIMS Data Entry/Review table. See LIMS manual for detailed procedure.

- Edit dilutions in DataTool or LIMS entry table as needed.

- Review results in the LIMS. Qualify and flag results in the LIMS Data Entry/Review table following Appendix R of the EPA Region 9 Laboratory Quality Assurance Plan.

8.4 Maintenance

The analyst should observe trends in the data such as declining response, erratic relative response, loss of classes of compounds, etc., which may signal the need for instrument maintenance. Document all routine maintenance or corrective actions taken in the maintenance logbook. Routine maintenance procedures and frequency are listed in Appendix G.

8.4.1 Entech Concentrator maintenance

Symptom:

- Decline in chloromethane, bromoform, chloroethane, and/or

1,2-dibromo-3-chloropropane responses or high %RSD for some of the compounds.

Possible Cause: Trap problem.
Corrective action: Replace trap if necessary.

- Carryover of high boiling analytes

  Possible causes: Cold spot in system, especially the transfer lines between the autosampler unit and the concentrator or between the concentrator and the GC.
  A sample containing high molecular weight components was analyzed on the system.

  Corrective action: Check temperatures of all heated zones. Adjust temperatures or replace heaters as required. Flush valve, gas lines, and sample lines with methanol or reagent water and bake out.

- Loss of sensitivity to selected analytes and increased pressure to maintain purge flow.

  Possible cause: Degradation of trap.
  Corrective action: Replace trap.

- Loss of all target analytes.

  Possible cause: Leak in system.

  Corrective action: Leak-check autosampler or concentrator system. Inspect quick connects and replace them when worn or distorted.

- Erratic Calibration for all very high and/or all very low boiling analytes coupled with acceptable calibration for other compounds:

  Possible cause: Dirty mass flow controller and/or Pump isolation valves.

  Corrective action: Turn off Entech autosamplers and concentrator power. Remove the right hand side cover of the concentrator (Entech 7100). Locate the Mass Flow Controller (MFC, stainless steel 3”x4”x2” box in the lower front end). The mass flow controller isolation valve is the valve closest to the MFC next to the inside wall (on the left). Carefully remove the clip holding the magnetic coil and remove the coil from the valve. Since the valve screws are easily stripped, care must be taken in removing and reinstalling them. Using an exact fit Philips screw driver, in good condition, carefully remove the 4 screws while firmly applying pressure to the top of screw driver to hold the screw driver in place. Carefully, remove the valve top cover which contains a cylinder and a spring. Sonicate the cylinder and spring in methanol for 1 hour. Carefully clean the inside of the valve with methanol wetted cotton swab. Dry the cylinder and spring at 100°C for 10 minutes. Reinstall the cylinder, spring, and cover. Reinstall screws by tightening each screw ½ turn each time then moving to the screw across (in the same as installing a car tire) until all screws are tightened. Do not over tighten the screws. Reinstall the magnetic coil. In instances of severe contamination, the Pump Isolation valve (right hand side by the MFC) may have to be cleaned in the same manner. Occasionally, the rubber seal on each end of the cylinder should be reconditioned by applying high viscosity pump oil after cleaning with methanol. Reinstall the concentrator cover. Turn the power back on to the autosampler then to the concentrator (must be done in this order). Restart the Entech software.

8.4.2 GC Maintenance

Symptom

- Carryover

  Possible causes: Analyzing a sample containing high molecular weight components or analyzing high-level and low-level samples sequentially.

  Corrective action: As necessary, replace inlet liner, clean inlet, bake out inlet, bake out column, clip column, replace septum, replace column.

- Shorter retention time.

  Possible cause: column flow rate problem.

  Corrective action: check flow rate and adjust as necessary.

- Longer retention time and/or smaller peaks.

  Possible causes: column flow rate problem, injection port leak, column butt connector leak, or column contamination.

  Corrective action: As necessary, check for leaks and replace septum. If issues remain, replace the column.

- Loss of resolution.

Possible causes: column flow rate problem, injection port leak, or column contamination.

Corrective action: Check for leaks and replace septum. If issues remain, replace the column.

8.4.3 MS maintenance:

Trend to be observed:

- Low m/z 502 to 69 ratio
- Failing tune checks
- Ion 75 in BFB ratio is increasing/failing

Corrective action: Clean the source.

9 QUALITY CONTROL

The EPA Region 9 Laboratory operates a formal quality control program and tracks compliance using the Lab QC Database. As it relates to this SOP, the QC program consists of a demonstration of capability, and the periodic analysis of MB, LCS, and other laboratory solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data that are generated. A summary of QC criteria is provided in Appendix C.

9.1 Demonstration of Capability

A Demonstration of Capability must be in place prior to using an analytical procedure and repeated if there is a change in instrument type, personnel, or method. Follow procedures described in EPA Region 9 Laboratory SOP 880 *Demonstration of Capability*.

9.2 Instrument QC

9.2.1 GC/MS System Performance Check (BFB analysis):

If the ion abundances fail to meet criteria listed in Appendix C, the BFB chromatogram should be examined for any obvious chromatographic problems. If the problem is determined to be related to poor chromatography, take the necessary corrective action and re-analyze the BFB. If the BFB continues to fail the ion abundance criteria, retune the mass spectrometer. It may be necessary to clean the ion source or take other corrective action to achieve the ion abundance criteria.

If a sample is injected after the time period listed in Appendix C, it must be re-analyzed.

9.2.2 Initial Calibration

Each GC/MS system must be calibrated whenever corrective action is performed which may change instrument response (e.g., ion source cleaning, column replacement, etc.) or if the continuing calibration verification acceptance criteria cannot be met.

The data system calculates the percent relative standard deviation (%RSD) of the RRF values for each compound using the following equation.

$$\%RSD = (SD/\ RRF_{avg}) \times 100$$

Where

$$SD = \sqrt{\frac{\sum_{i=1}^{n} (x_i - x_{ave})^2}{n - 1}}$$

The %RSD and SCV recovery requirements are listed in Appendix C.

If an ICAL fails because of one standard, a fresh solution of that standard may be re-analyzed and substituted for the standard that failed in the ICAL. If the failure is repeated (or the problem is not isolated to one calibration point), the system must be repaired so that the criteria are satisfied before any samples are analyzed.

If SCV criteria (see Appendix C) are not met, the SCV must be re-analyzed. If it fails again, prepare a fresh solution. Before continuing with analysis, take corrective action as needed, including reanalysis or re-preparation and reanalysis of the initial calibration if necessary.

9.2.3 Continuing Calibration Verification (may also be evaluated as the LCS)

Examine the areas of the quantitation ions of the internal standards in the calibration verification standard. If the area for any internal standard does not meet the recovery criteria listed in Appendix C, the CCV may be re-analyzed. If the failure is repeated, the analysis shall be terminated, the problem corrected, and a new calibration curve prepared.

Examine retention time of the internal standards in the calibration verification standard. If the retention time for any internal standard does not meet the criteria listed in Appendix C, then the chromatographic system must be inspected for malfunctions and corrections must be made, and a new calibration curve prepared.

The data system calculates the percent deviation (%D) of the RF values for each compound using the following equation:

$$\%D = \frac{RRF_c - RRF_{avg}}{RRF_{avg}} \ x\ 100$$

Where:

RRF_C: Relative Response Factor of compound c.
RRF_{avg}: Average Relative Response Factor

Qualify and flag results in the LIMS Data Entry/Review table following Appendix R of the EPA Region 9 Laboratory Quality Assurance Plan.

If the continuing calibration does not meet %D criteria listed in Appendix C, the analysis shall be terminated, the problem corrected, and a new continuing calibration analyzed.

9.2.4 Quantitation Limit Standard (CRL or QLS)

CRL must be analyzed at the beginning of the analytical run (typically just after the BFB and CCV). The QLS concentrations match the QL concentration (at the instrument). The recovery of analytes in the QLS is calculated as:

$$\%R = \frac{M}{T} \times 100$$

Where

%R	=	percent recovery of the standard.
M	=	measured concentration of the analyte, ug/L.
T	=	true concentration of the analyte in ug/L.

Generate a QLS custom report in ChemStation. Check that recoveries meet criteria specified in Appendix C.

Qualify and flag results in the LIMS Data Entry/Review table following Appendix R of the EPA Region 9 Laboratory Quality Assurance Plan.

If the QLS recovery does not meet criteria provided in Appendix C, rerun the QLS once to verify. If still unacceptable, determine the cause and take corrective action.

9.3 Batch QC

9.3.1 Method Blank (equivalent to an instrument blank in this procedure)

Analyze method blanks at the frequency listed in Appendix C. MB values $\geq$½ QL indicate potential laboratory contamination. Use the following guidelines to determine when samples must be re-prepared and re-analyzed:

1. If the MB analyte value $\geq$½ QL and the sample result is less than five times the MB analyte amount, reanalyze all associated samples containing less than five times the MB analyte amount.
2. If the MB analyte value $\geq$½ QL and the sample result is greater than five times the MB analyte concentration or is non-detected, report sample result without qualification.

9.3.2 Laboratory Control Sample (equivalent to the CCV in this procedure - one analysis serves both functions)

Analyze LCS at the frequency listed in Appendix C. LCS recovery is calculated as:

$$\%R = \frac{C_m}{C_t} \times 100$$

Where

$\%R$ = percent recovery.
C_m = measured analyte concentration in the LCS.
C_t = true analyte concentration in the LCS.

Generate a LCS custom report in ChemStation. Check that recoveries meet criteria specified in Appendix C.

Qualify and flag results in the LIMS Data Entry/Review table following Appendix R of the EPA Region 9 *Laboratory Quality Assurance Plan*.

If the LCS recovery does not meet criteria provided in Appendix C, rerun the LCS once to verify. If still unacceptable, determine the cause, take corrective action, and re-analyze the LCS and associated samples.

9.3.3 Matrix Duplicate

Analyze matrix duplicate (MD) at the frequency listed in Appendix C.

Calculate the relative percent difference (RPD) using the following equation:

$$RPD = \frac{|Cmd - C|}{(Cmd + C)/2} \times 100$$

Where

RPD	=	relative percent difference.
C_{md}	=	measured concentration in the MD, corrected dilutions.
C	=	measured concentration in the routine sample, corrected for dilutions.

The RPD limit for all analytes is $\leq$20. If the control limits are exceeded, flag all associated analyte results in the MD source sample as estimated (J).

9.4 Sample QC

9.4.1 Internal Standard Area:

Evaluate the internal standard areas in all field and QC samples immediately after analysis.

The internal standard areas must be within QC limits outlined in Appendix C.

Take the following steps if the internal standard areas are not within the limits:

1. Check the system performance.
2. Re-analyze the sample if a system performance problem is not evident. The sample may be diluted for re-analysis if examination of the chromatogram so indicates.

If the internal standard areas of the re-analysis are within limits, the problem was within the laboratory's control. Report the results from the re-analysis and submit the data from both analyses. Distinguish between the analysis and re-analysis by adding an "RE" suffix to the sample ID on the re-analysis. The problem must be documented in the LIMS work order memo field.

If the re-analysis does not solve the problem, report the results from the first analysis and submit the data from both analyses. Distinguish between the original analysis and the re-analysis by adding the "RE" suffix to the sample ID in the re-analysis.

9.5 Method Performance

Appendix H provides a summary of method performance at the 95% confidence level (2σ) based on EPA Region 9 Laboratory data.

Functional areas of the SOP that may be significant sources of analytical error are:

1. Sample degradation. Samples must be stored as outlined in the SOP to minimize losses.
2. Poor column condition may results in inadequate analyte separation and inaccurate integration.
3. Trap condition.
4. Leaks in sample transfer and GC/MS systems.

10 DOCUMENTATION

10.1 Standards

All standards (ICAL, ICV/CCV, QL, and LCS) are recorded in the LIMS. A copy of each Analytical Standard Record associated with sample analysis must be included in the data package.

10.2 Reagents

Record all reagents used for each analytical batch in the LIMS.

10.3 Analytical sequence

The analytical sequence is documented in the LIMS or in the instrument Run Log. Case Number, SDG number, date of analysis, QC solution IDs, analyst initials, lab sample IDs, client sample IDs, dilution factors and comments, if any, are recorded.

10.4 Analytical Report and Data Package

Analytical reports are produced using the LIMS. The data package is produced from LIMS and manual log records. EPA Region 9 Laboratory SOP 845 *Analytical Data Review* provides the typical format for data package deliverables.

10.5 Maintenance Logbook

Maintain a maintenance logbook for each instrument covered in this SOP. Document the following:

- Initial installation and performance
- Subsequent instrument modifications and upgrades, including major software upgrades

- All preventive or routine maintenance performed including repairs and corrective or remedial actions. Whenever corrective action is taken, record the date, the problem and resolution, and documentation of return to control.

All entries should be made in accordance with EPA Region 9 Laboratory SOP 850, *Notebook Documentation and Control.*

10.6 SOP Distribution and Acknowledgement

After approval, distribute an electronic copy of the final SOP to all laboratory staff expected to perform the SOP or review data generated by the SOP. (The Lab QC Database contains a list of assigned analysts for each SOP). All approved EPA Region 9 Laboratory SOPs are maintained in the LotusNotes database in Adobe Acrobat portable document format.

Analyst training is documented via the Training Record form and the Read and Understood Signature log; the latter is entered into the Lab QC Database.

10.7 SOP Revisions

Revisions to this SOP are summarized in Appendix J.

11 REFERENCES

EPA Region 9 Laboratory documents (SOPs, the Laboratory Quality Assurance Plan, etc.) are not included in this list. Analysts are referred to the SOP database on LotusNotes or the local area network (G:\USER\SHARE\QA PROGRAM\LAB SOPS PDF) for these documents; laboratory users should contact the Chemistry Team Leader or Laboratory QAO for copies of any supporting documents.

Agilent Technologies EnviroQuant ChemStation User's Guide.

Agilent Technologies, Agilent 6890 Series Gas Chromatograph Operating Manuals

Agilent Technologies/HP 5973 GC/MS User's Manual.

Entech Instruments Air Academy Course Manual.

Entech Instruments, Inc.; 7000 Operators Manual; Version 1.1.

EPA Method 0040, *Sampling of Principal Organic Hazardous Constituents from Combustion Sources Using Tedlar Bags.*

USEPA; Compendium Method TO-14; *Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using SUMMA7 Passivity Canister Sampling and Gas Chromatographic Analysis. May 1988.*

USEPA; Compendium Method TO-15; *Determination of Volatile Organic Compounds (VOCs) in Soil gas Collected in Specially-Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS)*; January, 1999.

APPENDIX A.
DEVIATIONS FROM THE REFERENCE METHOD

1. The applicability of this SOP has been extended to include analysis of samples collected in Tedlar bags.

2. The applicability of this SOP has been extended to cover analytes not listed in method TO-15.

3. Method TO-15 does not explicitly include holding times for samples in canisters. This SOP specifies a holding time of 30 days based on studies referenced in Method TO-15 that indicate stable storage of up to 30 days for most VOCs. The holding time for Tedlar bags is based on information provided in EPA Method 0040, *Sampling of Principal Organic Hazardous Constituents From Combustion Sources Using Tedlar Bags*.

4. This SOP allows for two compounds in the daily calibration to exceed the %D limit of ± 30%. However, the two compounds may not exceed a %D of ± 40%. Method TO-15 does not provide this exception.

5. Section 10.5.5.2 of TO-15 states that the "RRT for each target compound at each calibration level must be within 0.06 RRT units of the mean RRT for the compound". This SOP does not include this requirement.

APPENDIX B.
ANALYTES AND QUANTITATION LIMITS

The following table provides the target analytes list for this SOP with the CAS number and quantitation limits.

Analyte	CAS	QL, pptv	QL, µg/m^3	Report
Vinyl chloride	75-01-4	50	0.13	X
1,3-Butadiene	106-99-0	50	0.11	X
Bromoethene	593-60-2	50	0.22	X
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	50	0.38	X
1,1-Dichloroethene	75-35-4	50	0.20	X
Dichloromethane	75-09-2	50	0.17	X
tert-Butyl methyl ether (MTBE)	1634-04-4	50	0.18	X
trans-1,2-Dichloroethene	156-60-5	50	0.20	X
Hexane	110-54-3	50	0.18	X
1,1-Dichloroethane	75-34-3	50	0.20	X
cis-1,2-Dichloroethene	156-59-2	50	0.20	X
Chloroform	67-66-3	50	0.24	X
1,1,1-Trichloroethane	71-55-6	50	0.27	X
Carbon tetrachloride	56-23-5	50	0.31	X
Benzene	71-43-2	50	0.16	X
1,2-Dichloroethane	107-06-2	50	0.20	X
Trichloroethene	79-01-6	50	0.27	X
1,2-Dichloropropane	78-87-5	50	0.23	X
Toluene	108-88-3	50	0.19	X
Tetrachloroethene	127-18-4	50	0.34	X
1,2-Dibromoethane (EDB)	106-93-4	50	0.38	X
Chlorobenzene	108-90-7	50	0.23	X
m&p-Xylene	179601-23-1	100	0.43	X
o-Xylene	95-47-6	50	0.22	X
Styrene	100-42-5	50	0.21	X
1,2-Dichlorobenzene	95-50-1	50	0.30	X
Naphthalene	91-20-3	50	0.26	

APPENDIX C.
QUALITY CONTROL MEASURES AND CRITERIA

Parameter	Frequency	Criteria
BFB	Once every 24-hours	See Table Below
IC % RSD(1)	As Needed	$\leq$ 30%
CCV %D(1)	Once every 24-hours	$\leq$ 30%
CCV IS Area	Once every 24-hours	$\pm$40% of IC
CCV IS Retention Time Drift	Once every 24-hours	0.33 minutes (20 sec.) from IC
LCS Recovery(2)	Once every 24-hours	See Table Below
MB	Once every 24-hours	<½ QL
QLS Recovery(2)	Once every 24-hours	60-140%
Matrix Duplicate, RPD(2)	Once Per SDG	$\leq$ 20%
Sample IS Area		$\pm$40% of CCV
Sample Retention Time Drift		$\pm$0.33 min. (20 sec.) from CCV
SCV %D(2)	One per ICAL	70-130%
DOC P&A % Recovery	Annually	70-130%

(1) Up to 2 compounds may exceed 30% to a limit of 40%.
(2) Up to 10% of the compounds may fail to meet these criteria.

<u>BFB ion abundance criteria</u>

Mass (m/z)	*Relative Ion Abundance Criteria*
50	8.0 – 40.0 percent of mass 95
75	30.0 – 66.0 percent of mass 95
95	Base peak, 100 percent relative abundance
96	5.0 – 9.0 percent of mass 95
173	< 2.0 percent of mass 174
174*	50.0 to 120.0 Percent of 95 (Mass 95 must be base peak)
175	4.0 – 9.0 percent of mass 174
176	93.0 to 101.0 percent of mass 174
177	5.0 – 9.0 percent of mass 176

*All ion abundances must be normalized to m/z 95, the nominal base peak, even though the ion abundance of m/z 174 may be greater than that of m/z

<u>Quantitation Ions and Internal Standards</u>

Analyte	IS Reference	Primary Ion, m/z	Secondary Ion(s), m/z
Vinyl chloride	1	62	64, 27
1,3-Butadiene	1	54	39, 53
Bromoethene	1	106	108. 27
1,1,2-Trichloro-1,2,2-trifluoroethane	1	151	101, 103
1,1-Dichloroethene	1	61	96, 98
Dichloromethane	1	49	84, 86
tert-Butyl methyl ether (MTBE)	1	73	57, 41
trans-1,2-Dichloroethene	1	61	96, 63

Analyte	IS Reference	Primary Ion, m/z	Secondary Ion(s), m/z
Hexane	1	57	43, 86
1,1-Dichloroethane	1	63	27, 65
cis-1,2-Dichloroethene	1	96	61, 98
Chloroform	1	83	85, 47
1,1,1-Trichloroethane	1	97	99, 61
Carbon tetrachloride	1	117	119, 121
Benzene	2	78	51, 77
1,2-Dichloroethane	2	62	27, 49
Trichloroethene	2	130	132, 95
1,2-Dichloropropane	2	63	41, 76
Toluene	3	91	92, 39
Tetrachloroethene	3	166	164, 131
1,2-Dibromoethane (EDB)	3	107	109, 27
Chlorobenzene	3	112	77, 114
m&p-Xylene	3	91	106, 105
o-Xylene	3	91	106, 105
Styrene	3	104	78, 103
1,2-Dichlorobenzene	3	146	111, 148
Naphthalene	3	128	127, 129
Internal Standards			
Bromochloromethane	1	49	130, 128
1,4-Difluoromethane	2	114	63, 68
Chlorobenzene-d5	3	117	82, 119

LCS and Duplicate QC Criteria (based on laboratory performance at 99% confidence)

Analyte	LCS Recovery, % Lower	Upper	Duplicate Precision, RPD
Vinyl chloride	74	128	20
1,3-Butadiene	71	127	20
Bromoethene	67	125	20
1,1,2-Trichloro-1,2,2-trifluoroethane	78	123	20
1,1-Dichloroethene	77	129	20
Dichloromethane	76	117	20
tert-Butyl methyl ether (MTBE)	63	111	20
trans-1,2-Dichloroethene	61	108	20
Hexane	66	115	20
1,1-Dichloroethane	76	133	20
cis-1,2-Dichloroethene	64	142	20
Chloroform	63	123	20
1,1,1-Trichloroethane	65	121	20
Carbon tetrachloride	69	121	20
Benzene	65	123	20
1,2-Dichloroethane	75	123	20

Analyte	LCS Recovery, % Lower	LCS Recovery, % Upper	Duplicate Precision, RPD
Trichloroethene	57	144	20
1,2-Dichloropropane	63	125	20
Toluene	68	119	20
Tetrachloroethene	67	123	20
1,2-Dibromoethane (EDB)	67	111	20
Chlorobenzene	57	126	20
m&p-Xylene	51	121	20
o-Xylene	57	118	20
Styrene	57	128	20
1,2-Dichlorobenzene	43	124	20
Naphthalene	70*	130*	20*

*Insufficient historical data exists to determine statistical limits for this compound.. Default control limits are provided.

APPENDIX D.
INSTRUMENT INFORMATION

ENETCH CONCENTRATOR/AUTOSAMPLER MODES OF OPERATION

The Entech concentrator supports three trapping modes, 1) Microscale Purge & Trap (MP&T), 2) Cold Trap Dehydration (CTD), and 3) Focus Only (INJ). Additionally, the concentrator supports two sample introduction modes (Ambient and Loop) within each trapping mode.

A. Microscale Purge & Trap

MP&T eliminates most of the water and CO2 from the sample without loss of the polar and non-polar compounds. MP&T utilizes 3-stages of preconcentration and is normally used for the analysis of most ambient air samples. The series of events are as follows:

1. Sample and standards are preconcentrated on module 1 cryogenically using glass beads
2. Module 1 is warmed to 10°C and slowly flushed with helium to deliver the VOCs to Module 2 while leaving most of the water behind.
3. The sub-ambient Module 2 trap (-30 deg. C) allows the CO2 to pass through it and out to the pump while trapping light to heavy VOCs.
4. The VOCs are thermally desorbed and back flushed off of Module 2 to the focuser (Module 3)
5. The focuser is rapidly heated to inject the sample. The GC is started.
6. Traps 1 and 2 are baked out to prepare for the next analysis.

B. Cold Trap Dehydration

CTD uses trapping temperatures from -10°C to -60°C for both Modules 1 and 2, and is preferred when analyzing samples high in CO2. In this mode, an empty trap is installed in module. The series of events are as follows:

1. Sample and standards are preconcentrated on module 1 & 2 simultaneously.
2. Module 1 is warmed to 10°C and slowly flushed with helium to deliver the VOCs to Module 2 while leaving most of the water behind.
3. The sub-ambient Module 2 trap (-30 deg. C) allows the CO2 to pass through it and out to the pump while trapping light to heavy VOCs.
4. The VOCs are thermally desorbed and back flushed off of Module 2 to the focuser (Module 3)
5. The focuser is rapidly heated to inject the sample. The GC is started.
6. Traps 1 and 2 are baked out to prepare for the next analysis.

C. Focus Only

INJ procedure is used to focus a sample that is at higher concentrations or which was preconcentrated externally. The use of this mode requires prior Technical Director's approval. For the purpose of this SOP, this mode will not be discussed further.

ENTECH CONCENTRATOR/AUTOSAMPLER METHOD PARAMETERS

Recommended Concentrator operating parameters

The operating parameters for the Entech concentrators. These parameters may vary slightly to optimize instrument responses.

Method Name: C:\Smart\TO15NA.CTD Software ver. 4.20
Report Date/time 10/17/2013 12:01:16 PM

Stream: Sample
Preflush (sec): 30
Trap (cc/min): 50
Volume (cc): 250

Stream: Internal Standard
Preflush (sec): 5
Trap (cc/min): 30
Volume (cc): 50

Stream: Analytical Standard
Preflush (sec): 5
Trap (cc/min): 50
Volume (cc): 0

Stream: Sweep/Purge
Preflush (sec): 10
Trap (cc/min): 60
Volume (cc): 50

Stream: M1 -> M2
Preflush (sec):
Trap (cc/min): 5
Volume (cc): 20

Module1:
Trap temp(C): -40 Preheat? Yes
Preheat temp(C): 12
Desorb temp(C): 12
Bake temp(C): 150
Bake time(Min): 7
Bulk1:
Trap temp(C): 40
Desorb temp(C): 40
Bake temp(C): 150

Module2:

Trap temp(C): -50 Preheat? No
Preheat temp(C): 50
Desorb temp(C): 180
Bake temp(C): 190
Desorb time(C): 3.5

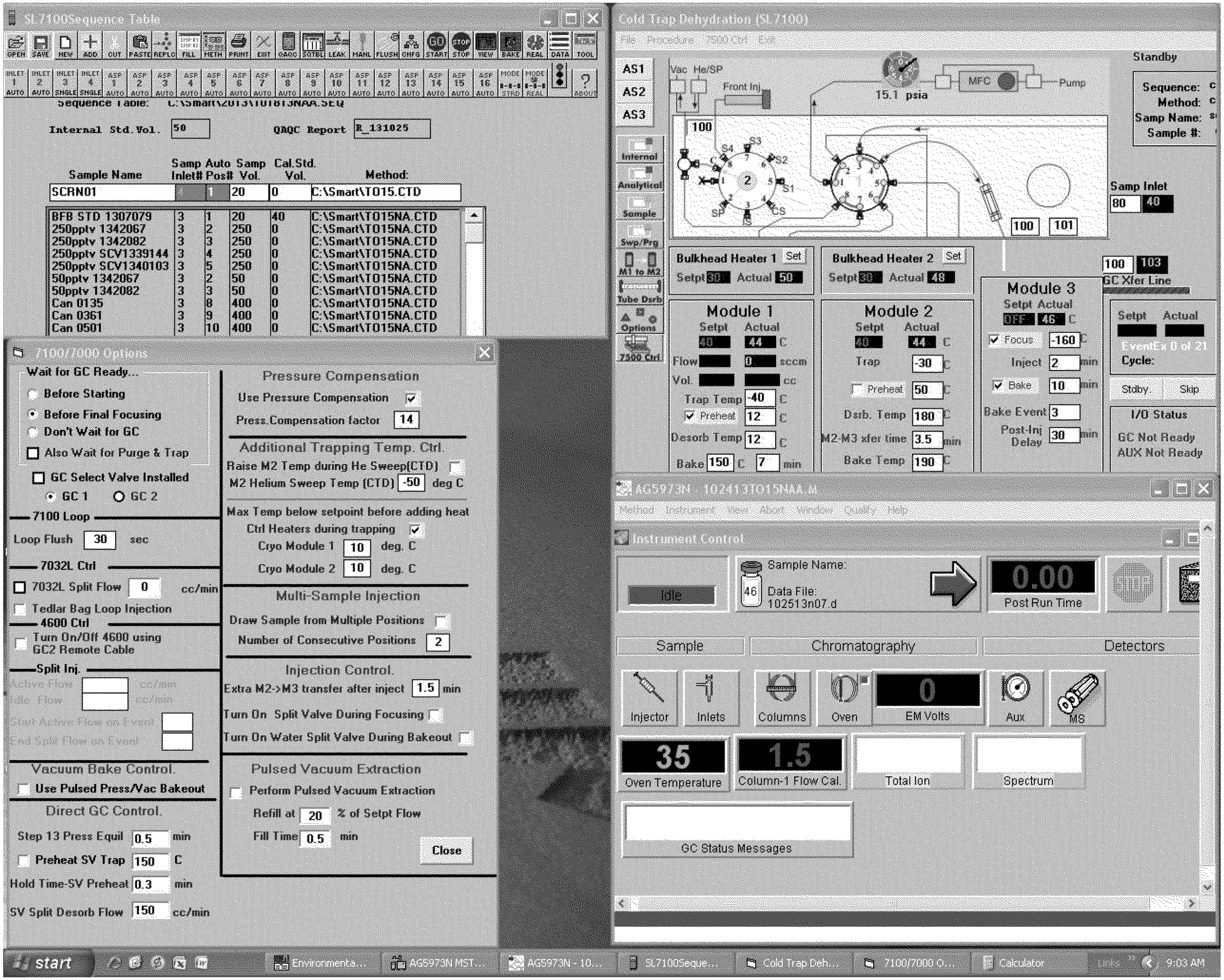
Bulk2:
Trap temp(C): 40
Desorb temp(C): 150
Bake temp(C): 150

Module3:
Trap temp(C): -160 Focus? Yes
Inject temp(C): 150
Inject time(Min):2
Bake temp(C): 100
Bake time(Min): 10
Bake on EventEx# : 3
Total Time (Min) : 30

Misc:
Sample Xfer temp(C): 80
GC Xfer temp(C): 100
MPOS Valve temp(C): 100

Wait for GC before injecting

Active GC: GC1
Pressure: 100
MPOS Valve temp(C): 100



RECOMMENDED GC/MSD PARAMETERS

HP/Agilent 6890 GC & HP/Agilent 5973MSD
The operating parameters for this system are listed below. Actual operating conditions may vary slightly to optimize instrument

INSTRUMENT CONTROL PARAMETERS

```
===================================================================
                    6890 GC METHOD
===================================================================

OVEN
  Initial temp:  35 'C (On)           Maximum temp:  250 'C
  Initial time:  10.00 min            Equilibration time:  0.50 min
  Ramps:
    #  Rate  Final temp  Final time
    1 10.00      240        0.50
    2   0.0(Off)
  Post temp:  240 'C
  Post time:  0.00 min
  Run time:  31.00 min

FRONT INLET (SPLIT/SPLITLESS)         BACK INLET (UNKNOWN)
  Mode:  Split
  Initial temp:  250 'C (On)
  Pressure:  8.42 psi (On)
  Split ratio:  20:1
  Split flow:  30.0 mL/min
  Total flow:  34.3 mL/min
  Gas saver:  On
  Saver flow:  20.0 mL/min
  Saver time:  2.00 min
  Gas type:  Helium

COLUMN 1                          COLUMN 2
  Capillary Column                  (not installed)
  Model Number:  Restek RTX-624
  RTX-624
  Max temperature:  250 'C
  Nominal length:  60.0 m
  Nominal diameter:  320.00 um
  Nominal film thickness:  1.80 um
  Mode:  constant flow
  Initial flow:  1.5 mL/min
  Nominal init pressure:  8.42 psi
  Average velocity:  31 cm/sec
```

Inlet: Front Inlet
Outlet: MSD
Outlet pressure: vacuum

FRONT DETECTOR () BACK DETECTOR ()

SIGNAL 1
Data rate: 20 Hz
Type: test plot
Save Data: Off
Zero: 0.0 (Off)
Range: 0
Fast Peaks: Off
Attenuation: 0

SIGNAL 2
Data rate: 20 Hz
Type: test plot
Save Data: Off
Zero: 0.0 (Off)
Range: 0
Fast Peaks: Off
Attenuation: 0

COLUMN COMP 1
(No Detectors Installed)

COLUMN COMP 2
(No Detectors Installed)

THERMAL AUX 2
Use: MSD Transfer Line Heater
Description:
Initial temp: 260 'C (On)
Initial time: 0.00 min

#	Rate	Final temp	Final time
1	0.0(Off)		

POST RUN
Post Time: 0.00 min

TIME TABLE

Time	Specifier	Parameter & Setpoint

7673 Injector

Front Injector:
No parameters specified

Back Injector:
No parameters specified

Column 1 Inventory Number :
Column 2 Inventory Number :

MS ACQUISITION PARAMETERS

General Information
------- -----------

Tune File : BFB102013NAA.U
Acquistion Mode : SIM

MS Information
-- -----------

Solvent Delay : 3.50 min

EM Absolute : False
EM Offset : 271
Resulting EM Voltage : 1364.7

[Sim Parameters]

GROUP 1
Group ID : C2&3
Resolution : Low
Plot 1 Ion : 54.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(27.0, 100) (39.0, 100) (53.0, 100)
(54.0, 100) (62.0, 100) (64.0, 100)

GROUP 2
Group ID : C4
Resolution : Low
Group Start Time : 7.00
Plot 1 Ion : 106.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(27.0, 100) (106.0, 100) (108.0, 100)

GROUP 3
Group ID : C5&6
Resolution : Low
Group Start Time : 8.95
Plot 1 Ion : 61.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(61.0, 100) (96.0, 100) (98.0, 100)
(101.0, 100) (103.0, 100) (151.0, 100)

GROUP 4
Group ID : C7

```
Resolution           : Low
Group Start Time       : 11.13
Plot 1 Ion           : 49.0
Ions/Dwell In Group     ( Mass, Dwell) ( Mass, Dwell) ( Mass, Dwell)
                  ( 49.0,   100) ( 84.0,   100) ( 86.0,   100)

GROUP 5
Group ID             : C8&9
Resolution           : Low
Group Start Time       : 11.76
Plot 1 Ion           : 61.0
Ions/Dwell In Group     ( Mass, Dwell) ( Mass, Dwell) ( Mass, Dwell)
                  ( 41.0,   100) ( 57.0,   100) ( 61.0,   100)
                  ( 63.0,   100) ( 73.0,   100) ( 96.0,   100)

GROUP 6
Group ID             : C10
Resolution           : Low
Group Start Time       : 12.36
Plot 1 Ion           : 43.0
Ions/Dwell In Group     ( Mass, Dwell) ( Mass, Dwell) ( Mass, Dwell)
                  ( 43.0,   100) ( 57.0,   100) ( 86.0,   100)

GROUP 7
Group ID             : C11
Resolution           : Low
Group Start Time       : 13.12
Plot 1 Ion           : 27.0
Ions/Dwell In Group     ( Mass, Dwell) ( Mass, Dwell) ( Mass, Dwell)
                  ( 27.0,   100) ( 63.0,   100) ( 65.0,   100)

GROUP 8
Group ID             : C12
Resolution           : Low
Group Start Time       : 14.56
Plot 1 Ion           : 61.0
Ions/Dwell In Group     ( Mass, Dwell) ( Mass, Dwell) ( Mass, Dwell)
                  ( 61.0,   100) ( 96.0,   100) ( 98.0,   100)

GROUP 9
Group ID             : C1&13&14
Resolution           : Low
Group Start Time       : 15.11
Plot 1 Ion           : 83.0
Ions/Dwell In Group     ( Mass, Dwell) ( Mass, Dwell) ( Mass, Dwell)
                  ( 47.0,   100) ( 49.0,   100) ( 61.0,   100)
                  ( 83.0,   100) ( 85.0,   100) ( 97.0,   100)
                  ( 99.0,   100) ( 128.0,   100) ( 130.0,   100)
```

GROUP 10
Group ID : C16
Resolution : Low
Group Start Time : 15.80
Plot 1 Ion : 117.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(117.0, 100) (119.0, 100) (121.0, 100)

GROUP 11
Group ID : C15&17&18
Resolution : Low
Group Start Time : 16.20
Plot 1 Ion : 78.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(27.0, 100) (49.0, 100) (51.0, 100)
(62.0, 100) (63.0, 100) (77.0, 100)
(78.0, 100) (88.0, 100) (114.0, 100)

GROUP 12
Group ID : C19
Resolution : Low
Group Start Time : 17.44
Plot 1 Ion : 130.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(95.0, 100) (130.0, 100) (132.0, 100)

GROUP 13
Group ID : C20
Resolution : Low
Group Start Time : 17.95
Plot 1 Ion : 63.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(41.0, 100) (63.0, 100) (76.0, 100)

GROUP 14
Group ID : C21
Resolution : Low
Group Start Time : 19.66
Plot 1 Ion : 91.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(39.0, 100) (91.0, 100) (92.0, 100)

GROUP 15
Group ID : C22
Resolution : Low
Group Start Time : 20.53
Plot 1 Ion : 166.0

```
Ions/Dwell In Group     ( Mass, Dwell) ( Mass, Dwell) ( Mass, Dwell)
                        ( 131.0,   100) ( 164.0,   100) ( 166.0,   100)

GROUP 16
Group ID            : C23
Resolution          : Low
Group Start Time    : 21.29
Plot 1 Ion          : 107.0
Ions/Dwell In Group     ( Mass, Dwell) ( Mass, Dwell) ( Mass, Dwell)
                        (  27.0,   100) ( 107.0,   100) ( 109.0,   100)

GROUP 17
Group ID            : C24&25&26&27
Resolution          : Low
Group Start Time    : 21.97
Plot 1 Ion          : 117.0
Ions/Dwell In Group     ( Mass, Dwell) ( Mass, Dwell) ( Mass, Dwell)
                        (  77.0,   100) (  82.0,   100) (  91.0,   100)
                        ( 105.0,   100) ( 106.0,   100) ( 112.0,   100)
                        ( 114.0,   100) ( 117.0,   100) ( 119.0,   100)

GROUP 18
Group ID            : C27&28
Resolution          : Low
Group Start Time    : 22.97
Plot 1 Ion          : 104.0
Ions/Dwell In Group     ( Mass, Dwell) ( Mass, Dwell) ( Mass, Dwell)
                        (  78.0,   100) (  91.0,   100) ( 103.0,   100)
                        ( 104.0,   100) ( 105.0,   100) ( 106.0,   100)

GROUP 19
Group ID            : C29
Resolution          : Low
Group Start Time    : 23.82
Plot 1 Ion          : 174.0
Ions/Dwell In Group     ( Mass, Dwell) ( Mass, Dwell) ( Mass, Dwell)
                        (  95.0,   100) ( 174.0,   100) ( 176.0,   100)

GROUP 20
Group ID            : C30
Resolution          : Low
Group Start Time    : 24.90
Plot 1 Ion          : 146.0
Ions/Dwell In Group     ( Mass, Dwell) ( Mass, Dwell) ( Mass, Dwell)
                        ( 111.0,   100) ( 146.0,   100) ( 148.0,   100)

GROUP 21
Group ID            : C31
```

Resolution : Low
Group Start Time : 26.65
Plot 1 Ion : 128.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(127.0, 100) (128.0, 100) (129.0, 100)

[MSZones]

MS Quad : 150 C maximum 200 C
MS Source : 230 C maximum 250 C

END OF MS ACQUISITION PARAMETERS

TUNE PARAMETERS

EMISSION : 34.610
ENERGY : 69.922
REPELLER : 34.814
IONFOCUS : 90.157
ENTRANCE_LE : 14.000
EMVOLTS : 1094.118
AMUGAIN : 2537.000
AMUOFFSET : 135.000
FILAMENT : 2.000
DCPOLARITY : 1.000
ENTLENSOFFS : 18.071
MASSGAIN : 141.233
MASSOFFSET : -10.445

END OF TUNE PARAMETERS

END OF INSTRUMENT CONTROL PARAMETERS

Analytical system preparation:

Leak Checking

1. Check that the MSD analyzer temperatures displayed as MS zones are set to the values specified in Appendix D

2. If the display indicates that the analyzer temperatures are not at the desired set points, perform corrective action according to the operator's manual.

3. Check the source analyzer pressure. The analyzer pressure should be less than 10^{-5} torr as indicated by the ion gauge controller. Values higher than indicated above are indicative of large leaks and must be corrected.

4. Check the nitrogen (m/z 28) to water (m/z 18) ratio as follow:

   From View menu in Instrument Control panel of the HP 5973 MSD Instrument, select Perform Diagnostic/Vacuum and then run the Air / Water program from Diagnostics menu. The Air and Water Check report will be printed out. Alternatively, set the mass spectrometer to scan over a range of 10 to 50 m/z. Observe the ratio of the water peak (m/z 18) to the nitrogen peak (m/z 28). If a leak is present in the mass spectrometer the nitrogen peak will be greater than the water peak. Corrective action must be taken if a leak is detected.

Auto Tuning

Perform an autotune of the analytical system prior to an initial calibration, whenever the mass spectrometer is shut down, or the source is cleaned. Perfluorotributylamine (FC43) is the compound used to perform the mass calibration of the instrument. Proper tuning of the instrument is necessary to produce standardized fragmentation patterns of target and non-target compounds.

Open the HP MSD Instrument Control window and choose the Instrument menu.
Select Perform MS Autotune.

The autotune software will adjust the mass ratio, abundance, peak shape, width, isotope peak resolution, and mass assignment.

An autotune report will be generated and the parameters will be saved in ATUNE.U.

The Agilent ChemStation software requires that the FC43 spectrum meet the following criteria:

Mass	Target % of Mass 69
50	0.3-5
69	100
131	20-120
219	20-120
414	0.3-10
502	0.3-10

Select Manual Tune from View menu in Instrument Control view and manually tune the MSD, using ATUNE.U as reference. Adjust the parameters of Ion Focus, Entrance Lens, Repeller, Entrance Lens Offset, EM voltage etc to suit your analysis needs.

Save the manual tune file in the format of month-date-year-sequential letter. For example: 082301A.U.

Mass Calibration:

Perform mass calibration of the analytical system at the start of each 24-hour analysis sequence, prior to an initial calibration, whenever the mass spectrometer is shut down, or whenever there is a mass miss-assignment is noted. Mass calibration is performed to ensure the accurate assignment of masses to ions generated in the ion volume of the mass spectrometer.

APPENDIX E
IN-HOUSE STANDARD PREPARATION

Existing VOC standards in methanol may be used to prepare gas phase standards. In preparing the standards, the following issues must be observed:

1. It was previously determined that the largest amount of methanol that may be introduced in the analytical system is 0.5 uL for each analytical run; therefore, it is necessary to minimize the amount of methanol used.
2. To facilitate mixing of the heavy boiling analytes, the can must be quickly pressurized while hot. Analyte condensation and erratic responses may result if the can is allowed to cool prior to re-pressurization.
3. Since most volatile standards are purchased at concentration of 2,000 ug/mL in methanol; intermediate standards must be made to avert having to measure ultra small quantities of standard solution. To reduce the amount of methanol, intermediate standards should be prepared in purged DI water.
4. Prepared standards should be allowed to equilibrate for a period of 24-hours.

Calculate the amount of methanol standard to be used as follow:

$$Vol_x = \frac{Fv * Fc * MW}{IC * 22.4}$$

Where

- Vol_x: Volume of methanol standard in uL.
- Fv: Final volume of prepared gas standard in Liter. For a 6 L cans, Fv is 12, 6L pressurized 2X.
- Fc: Final concentration of gas standard in ppbv.
- MW: Molecular weight of compound in grams/mole
- IC: Initial concentration of methanol standard in ug/mL. Since most volatile standards are purchased at concentration of 2,000 ug/mL, IC = 2000

Prepare an intermediate standard as follow:

1. Pressurize a clean can to 15-16 psia with zero air
2. Open the valve to allow the pressure to return to 1 atmosphere
3. Remove the valve from the can
4. Inject the standard, as calculated above, in the canister at ambient pressure
5. Quickly reconnect the canister valve
6. Tightly cap the canister and place in a 120ºC oven for 1 hour.
7. To facilitate mixing of the heavy boiling analytes, the can is removed from the oven, connected to the diluter, and quickly pressurized to 30 psia while warm
8. The can is allowed to equilibrate back to room temperature
9. The can is re-pressurized to 2X atmosphere to compensate for the drop in pressure due to cooling

The conversion from ug/mL to ppbv was achieved using the following formula:

$$Fc = \frac{Volx}{Fv\ L\ Air} \quad \frac{IC\ ug}{mL} \quad \frac{1mL}{1000\ uL} \quad \frac{10^{-6}\ g}{1\ ug} \quad \frac{1\ mole}{(MW)\ gx} \quad \frac{22.4\ L\ air}{Mole\ air} \quad \frac{ppb}{10^{-9}}$$

Example:

The following additional TO15 compounds were required for a project
1,2-Dibromo-3-chloropropane
1,2,3-Trichloropropane

1. 1 ppmv Subset Standard (LIMS ID 9D13007) Used to prepare levels 1, 2, and 5 ppbv via the loop injection:

   The standard was prepared by injecting 7 uL of 2,000 ug/mL 1,2,3 TCP (LIMS ID 8J29019) and 10 uL of 2000 ug/mL DBCP (LIMS ID 8J29020) added into 1L can @ ambient pressure. Heated for 1/2 hour @ 99.9 degree C then pressurize up to 29.9 psi while hot. The can was allowed to reach room temperature then re-pressurized to 29.9 psi to compensate for the drop in pressure due to cooling.

2. 20 ppbv Calibration Standard (LIMS ID 9D10020) Used to prepare levels 10, 15, and 20 ppbv via the ambient injection:

   An intermediate standard was prepared by mixing 80 uL of 2,000 ug/mL 1,2,3 TCP (LIMS ID 8J29019) and 120 uL of 2000 ug/mL DBCP (LIMS ID 8J29020) into 800 uL of purge and trap grade methanol. The resulting mix was assigned LIMS id 9D09012.

   20 uL aliquot of intermediate standard (LIMS ID 9D09012) was added into 6L can @ ambient pressure. Heated for 1/2 hour @ 99.9 degree C then pressurize up to 29.9 psi while hot. The can was allowed to reach room temperature then re-pressurized to 29.9 psi to compensate for the drop in pressure due to cooling.

   The can was vented in a hood down to ambient pressure (10 uL of original standard remains). The primary standards (LIMS ID 8G16008 @ 100 ml/min, and zero air @ 2400 ml/min) were then introduced in the same can to a final pressure of 29.9 psi.

3. 20 ppbv LCS Standard (LIMS ID 9D13014):

   An intermediate standard was prepared by mixing 200 uL of 200 ug/mL 1,2,3 TCP (LIMS ID 9C18006) and 25 uL of 2000 ug/mL EDB/DBCP (LIMS ID 9C18007). The resulting mix was assigned LIMS id 9D10019.

   20 uL aliquot of intermediate standard (LIMS ID 9D10019) was added into 6L can @ ambient pressure. Heated for 1/2 hour @ 99.9 degree C then pressurize up to 29.9 psi while hot. The can was allowed to reach room temperature then re-pressurized to 29.9 psi to compensate for the drop in pressure due to cooling.

   The can was vented in a hood down to ambient pressure. The primary standard (LIMS ID 8J02008 @ 400 ml/min, and zero air @ 600 ml/min) were then introduced in the same can to a final pressure of 29.9 psi.

The conversion from ug/mL to ppbv was achieved using the following formula:

20 uL Conc x ug 1mL 10^{-6} g 1 mole 22.4 L air ppb

Fv L Air mL 1000 uL 1 ug gx (MW) Mole air 10^{-9}

Or $$\frac{448 * \text{Conc x (ug/mL)}}{\text{Fv} *(\text{MWx})}$$

Attached is a table of the standards utilized and the final calculated concentration of each target analyte in ppbv.

Compound	MW
1,2-Dibromoethane (EDB)	187.86
1,2,3-Trichloropropane	147.43
1,2-Dibromo-3-chloropropane	236.33

1 ppmv Subset Standard (LIMS ID 9E12013)

Compound	MW	Initial Volume (uL)	Initial Concentration (ug/mL)	Final Volume (L)	Final Concentration (PPBV)
1,2,3-Trichloropropane	147.43	420	200	12	1063.56
1,2-Dibromoethane (EDB)	187.86	60	2000	12	1192.38
1,2-Dibromo-3-chloropropane	236.33	60	2000	12	947.83

Intermediate Standard (LIMS ID 9E12014)

Compound	Initial Volume (uL)	Initial Concentration (ug/mL)	Final Volume (uL)	Final Concentration (ug/mL)
1,2,3-Trichloropropane	80	2000	1000	160.00
1,2-Dibromo-3-chloropropane	120	2000	1000	240.00

20 ppbv Calibration Standard (LIMS ID 9E12016)

Compound	MW	Initial Volume (uL)	Initial Concentration (ug/mL)	Final Volume (L)	Final Concentration (PPBV)
1,2,3-Trichloropropane	147.43	20	160.00	24	20.26
1,2-Dibromo-3-chloropropane	236.33	20	240.00	24	18.96

Intermediate LCS Standard (LIMS ID 9E12015)

Compound	Initial Volume (uL)	Initial Concentration (ug/mL)	Final Volume (uL)	Final Concentration (ug/mL)
1,2,3-Trichloropropane	80	2000	1000	160.00
1,2-Dibromo-3-chloropropane	120	2000	1000	240.00

20 ppbv LCS Standard (LIMS ID 9E12017)

Compound	MW	Initial Volume (uL)	Initial Concentration (ug/mL)	Final Volume (L)	Final Concentration (PPBV)
1,2,3-Trichloropropane	147.43	20	160.00	24	20.26
1,2-Dibromo-3-chloropropane	236.33	20	240.00	24	18.96

APPENDIX F.
DILUTION LOGBOOK, EXAMPLE

AIR/SOIL GAS DILUTION LOG

DATE/ INITIAL	TIME	LAB SAMPLE #	CLIENT SAMPLE #	CAN ID	INITIAL PRESSURE (PSI)	INITIAL VOL (mL)	FINAL VOL (mL)	FINAL PRESSURE (PSI)	AMBIENT PRESSURE (PSI)	DILUTION FACTOR

USEPA REGION 9 LABORATORY

APPENDIX G.
PREVENTATIVE MAINTENANCE REQUIREMENTS

GC Maintenance

Item	Frequency	Actions/Comments
Split vent trap	As Needed	Replace.
Inlet Hardware	Annually	Check for leaks and clean. Check parts and replace when parts are worn, scratched, or broken.
Inlet Septum	As Needed	Replace ferrules when changing columns and/or inlet parts
Column Maintenance	As Needed	Remove 1/2-1 meter from the front of the column when experiencing chromatographic problems (peak tailing, decreased sensitivity, retention time changes, etc.).
Column Replacement	As needed	When trimming and/or solvent rinsing no longer return chromatographic performance.
Ferrules/Column Union	As needed	Replace ferrules when changing columns and/or inlet parts.
Purge/Sample Lines	As needed	Bake out and purge. Clean with organic free water if necessary.
Trap	As needed	Replace when loss of performance.
EM voltage	As needed	If an overall change in sensitivity (area counts in CCV in comparison to most recent ICAL), the EM voltage may need adjusting.

MS Maintenance

Task	Every Week	Every 6 Months	Every Year	As Needed
Tune the MSD				☐
Check the foreline pump oil level	☐			
Check the calibration vials		☐		
Replace the foreline pump oil		☐		
Clean the ion source				☐
Check the carrier gas traps on the GC				☐
Replace worn out parts				☐
Lubricate sideplate or vent valve O-rings				☐

APPENDIX H.
METHOD PERFORMANCE

Analysis of Volatile Organic Compounds in Air by GC/MS SIM November 2012 – October 2013

Analyte	Number of Measurements	Mean Recovery, %	Standard Deviation (σ)	95% Confidence Interval (2 σ)	
Vinyl chloride	24	101	9.13	83	119
1,3-Butadiene	24	99	9.49	80	118
Bromoethene	24	96.3	9.71	77	116
1,1-Dichloroethene	24	103	8.75	85	120
1,1,2-Trichloro-1,2,2-trifluoroethane	24	100	7.61	85	116
Dichloromethane	24	96.5	6.97	83	110
trans-1,2-Dichloroethene	24	84.7	7.87	69	100
tert-Butyl methyl ether (MTBE)	24	87.3	7.98	71	103
Hexane	24	90.4	8.21	74	107
1,1-Dichloroethane	24	105	9.61	85	124
cis-1,2-Dichloroethene	24	103	13.1	77	129
Chloroform	24	93.1	9.99	73	113
1,1,1-Trichloroethane	24	93.3	9.3	75	112
Carbon tetrachloride	24	95.1	8.8	78	113
1,2-Dichloroethane	24	98.6	8.05	83	115
Benzene	24	93.8	9.7	74	113
Trichloroethene	24	100	14.5	71	130
1,2-Dichloropropane	24	94	10.4	73	115
Toluene	24	93.4	8.46	76	110
Tetrachloroethene	24	95.3	9.41	76	114
1,2-Dibromoethane (EDB)	24	88.9	7.27	74	103
Chlorobenzene	24	91.1	11.5	68	114
m&p-Xylene	24	86.1	11.8	63	110
o-Xylene	24	87.3	10.2	67	108
Styrene	24	92.5	11.7	69	116
1,2-Dichlorobenzene	24	83.3	13.6	56	110

APPENDIX I.
CHEMSTATION FILENAMING CONVENTIONS

Files for data, methods, tunes, and sequences on ChemStation computers and the LAN are named using the following naming conventions:

Directories

On the Workstation (When available, use D: drive):

Data:	C:\MSDCHEM \1\DATA\YEAR\DATA\MMDDYYSS or D:\MSDCHEM\YEAR\DATA\MMDDYYSS
Methods:	C:\MSDCHEM\1\DATA\YEAR\METHODS or D:\MSDCHEM\YEAR\METHODS
Sequences:	C:\MSDCHEM\1\DATA\YEAR\SEQUENCE or D:\MSDCHEM\YEAR\SEQUENCE
Tunes:	C:\MSDCHEM\1\5973N or C:\MSDCHEM\1\5975

On the LAN:

Data:	I:\DATA\ROOM NUMBER\INSTRUMENT\YEAR\DATA\MMDDYYSS
Methods:	I:\DATA\ROOM NUMBER\INSTRUMENT\YEAR\METHODS
Sequences:	I:\ DATA\ROOM NUMBER\INSTRUMENT\YEAR\SEQUENCE
Tunes:	I:\ DATA\ROOM NUMBER\INSTRUMENT\YEAR\TUNE

Methods
MMDDYYATC

Sequence
MMDDYYCSS

Data Files
MMDDYYCSS

Tune Files
MMDDYYA

Variables

A: Enter analysis, as follow:

504	EDB
TO15	TO15
BNA	BNA
BNA (SIM)	PAH or PCP
PEST	PEST
PCB	PCB
RSK175	RSK
TPH-G	GRO
TPH-D	DRO
VOA	VOA
BFB	BFB

	DFTPP	DFT
C:	Channel (use when applicable):	
	Front	A
	Back	B
	Both	AB
DD:	Day	i.e. 01, 02, 03, ….
MM:	Month	i.e. 01, 02, 03, ….
SS:	Sequential number 01, 02, 03, ….	
T:	Matrix Type (if applicable)	
	Water	W
	Solid	S
	Air	A
	Oil	O
	Other	X
YY:	Year	i.e. 13 for 2013

APPENDIX J.
REVISION HISTORY

STANDARD OPERATING PROCEDURE: 314
Revision: 4, Effective: 2/20/2014

LOW LEVEL ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN AIR BY GC/MS SELECTED ION MONITORING

Revision	Effective Date	Description
2	09/11/2009	Updated analyte list and references
3	02/15/2013	1. Added guidance on sample dilutions, Section 8.3.8 2. Clarified BFB QC criteria and included language stating daily sequence procedures and guidelines, 9.2.2 3. Updated QC criteria table in Appendix C 4. Updated Table 9.6, Method Performance 5. Updated Appendix B,C to include extended list of target analytes 6. Added language specifying minimum and maximum volume loads as prescribed by manufacturer for the Entech pre-concentrator, Section 5.1 7. Added SOP31 1 to references list 8. Added statement describing where canister pressures are recorded, 5.3 9. Revised Calibration Gas Standards list, vendors, etc., 7.3 10. Corrected BFB conversion equation, 7.3.5 11. Corrected Calibration concentration point, 7.3.8 12. Clarified definition and purpose of LCS for this analysis, 8.2.4 13. Removed "bracketing" QLS criteria in section 8.2.5 and made the CCV the new bracketing standard 14. Added language for sample prep, canister equilibration step, 8.3.1 15. Clarified language on Mass calibration and added tune file description, 9.2.1 16. Added guidelines and corrective action procedures for proper ICAL determination 9.3.1 17. Added language describing new "bracketing" CCV criteria ,9.4.1 18. Added language describing updated LCS QC requirements and clarified corrective action procedures,9.4.2 19. Added QCS corrective action procedure, 9.4.3 20. Clarified Method Blank language and corrective action guidelines, 9.4.4. 21. Removed section 9.4.6 which describes Matrix Spike/Spike Duplicate procedures that are not applicable 22. Updated LCS limits and Method Performance Limits in

Revision	Effective Date	Description
		Appendices 23. Modified Appendices
4	2/20/2014	1. Incorporated the use of internal standard calibration 2. Combined CCV and LCS into one analysis. 3. Changed peak ratio requirement to match reference method. 4. Edited throughout for accuracy and clarity and current laboratory SOP requirements.